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(54) COMPLEX ALUMINIUM PHOSPHATES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel phosphates and to their preparation, and in particular to complex phosphates of aluminium. We have found that certain complex phosphates of aluminium are especially useful for preparing fibres, coatings, binders and fine particles of aluminium phosphate.

According to the present invention there is provided halogen-containing complex phosphate of aluminium containing at least one ferred as the hydroxy compound since compound R—OH wherein A is an organic group.

The term "phosphate" includes acid phosphates but does not include phosphate esters.

It is preferred that R be an aliphatic hydrocarbon group or a substituted aliphatic hydrocarbon group, for example wherein the substituent is one or more of the following: phenyl, hydroxyl, carboxyl or alkoxy. Unsubstituted aliphatic alcohols are especially preferred as the hydroxy compound since complex phosphates according to the invention containing them are easily separated solids obtainable in high yield. We have found that aliphatic alcohols containing one to ten carbon atoms are especially suitable, and owing to their ready availability we prefer to use aliphatic alcohols containing from one to four carbon atoms, for example, methanol, ethyl alcohol, n-propyl alcohol or isopropyl alcohol. In preferred embodiments of the invention, ethyl alcohol is used, as the complex phosphates containing it are especially readily formed as solids in high yield.

The halogen in the halogen-containing complex phosphate of aluminium is preferably chlorine, but the compounds may contain other halogens, for example bromine or iodine.

The ratio of the number of gram atoms of

aluminium to the number of gram atoms of phosphorus in the complex phosphates of aluminium may vary over a wide range, for example from 1:2 to 2:1, but is preferably substantially 1:1 as complex phosphates of the invention having this ratio decompose at low temperatures directly to form aluminium orthophosphate having greater chemical stability and refractoriness than aluminium phosphate formed from complex phosphates with other ratios. The ratio of the number of gram atoms of aluminium to the number of gram atoms of halogen in the complex phosphates is preferably substantially 1:1.

The complex phosphates of the invention may be monomeric or polymeric.

The structure of the complex phosphates is not fully understood and some of the chemically-bound hydroxy compounds may be bound as groups —OR rather than as complete molecules.

The monomeric forms, or the repeating units of the polymeric forms of the complex phosphates, may contain, for example, from one to five molecules of the hydroxy compound. Most frequently the number of molecules of the hydroxy compound is 4. In some cases the complex phosphates may contain molecules of different hydroxy compounds, for example they may contain both chemically-bound water and a chemically-bound organic hydroxy compound, the total number of such molecules being, for example, from 2 to 5.

An example of a complex phosphate according to the invention is the complex phosphate containing ethyl alcohol and having the empirical formula $AlPClH_2C_6O_8$. The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium chlorophosphate ethanolate, for convenience referred to herein as ACPE, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

A further example of a complex phosphate is that containing bromine and ethyl alcohol having an empirical formula $AlPBrH_2C_6O_8$.

The infra-red and X-ray characteristics of the compound are as hereinafter described. This compound is designated aluminium bromophosphate ethanolate, for convenience referred to as ABPE, but it is to be understood that this designation in no way implies any particular molecular structure for the compound.

The complex phosphates are generally soluble in water and organic solvents, especially polar organic solvents. Solvents comprising water and a water-miscible organic solvent are especially convenient for dissolving the complex phosphates. Solubility generally increases as the pH of the solution is decreased, and it is preferable to establish a pH of less than 2.5 in water solutions to maintain maximum solubility. The compounds of the invention generally give viscous solutions in water.

Thus the invention also provides a method of preparing a homogeneous composition comprising a phosphate of aluminium and an organic solvent which comprises dissolving a complex phosphate of the invention in an organic solvent. The composition may contain water or it may be substantially anhydrous. The organic solvent is preferably a liquid at ordinary temperatures. The organic solvent is preferably a polar solvent, especially an oxygen-containing polar solvent. Especially useful are aliphatic alcohols containing up to 10 carbon atoms, esters, polyhydric alcohols, and glycol esters. Most preferred are aliphatic alcohols containing from 1 to 5 carbon atoms, for example methanol or ethanol. The solvent may be a mixture of solvents. The ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus in the composition may vary over a wide range, for example from 1:2 to 1.5:1, but is preferably substantially 1:1, as aluminium phosphate formed by decomposition of a composition having this ratio is especially stable.

The complex phosphates of the invention or a mixture containing the said complex phosphate, for example their solutions, may be prepared, for example, by reacting aluminium or an aluminium compound, preferably a halide, with an organic hydroxy compound R-OH and phosphoric acid. If desired, the phosphoric acid may be formed in situ by using a compound capable of forming phosphoric acid under the reaction conditions, for example phosphorus pentoxide, phosphorus oxyhalides and phosphorus halides may be used in the presence of water. The aluminium halide may be a simple halide or an oxyhalide or an aluminium alkoxy halide, for example aluminium ethoxy chloride. Other suitable aluminium compounds include aluminium alkoxides, for example aluminium ethoxide. When aluminium or an aluminium compound other than a halide is used, the presence of a halogen acid is necessary. Mixtures of hydroxy compounds may be used. An aqueous solution of phosphoric acid may be used, conveniently an 88%

solution in water, although it is preferred to ensure that no more than about 5% by weight of water based on the total weight of reaction mixture is present when a complex phosphate containing an organic hydroxy compound is prepared, thereby avoiding a loss of yield.

The order in which the reactants are added to one another is not critical; we prefer to add the aluminium compound to the hydroxy compound and then to react the phosphoric acid with the resultant mixture. It may be convenient to dissolve the aluminium compound in a suitable solvent, which may be either the hydroxy compound or an inert solvent, before reacting it further. This is especially convenient when the hydroxy compound is a solid at the temperature at which the reaction is carried out or when it is a poor solvent for the aluminium compound.

The highest yields of product are obtained when the molar ratio of aluminium to phosphorus in the reaction is substantially 1:1.

The reaction may be carried out over a wide range of temperature, but generally we prefer to use a temperature below 60°C and preferably from 0°C to 50°C, to obtain optimum yields.

It is preferred, for example when it is desired to preserve anhydrous conditions, to carry out the reaction in an atmosphere of a dry inert gas, for example, nitrogen.

Complex phosphates according to the invention containing chemically-bound water molecules or a mixture containing the said complex phosphate may also be prepared by the hydrolysis of another complex phosphate of the invention which contains a chemically-bound organic hydroxy compound, or by carrying out the reactions hereinbefore described in the presence of water. By this means it is possible to replace partially the organic hydroxy compound with water molecules. (The complete replacement of the organic hydroxy compound by water molecules is also possible by hydrolysis and is described and exemplified in our copending application 1737/73 (Serial No. 1,322,724) which has been divided out of the present application.) It is especially convenient to use as starting material the complex phosphate having the empirical formula $\text{AlPClH}_{2.2}\text{C}_2\text{O}_5$. The partially hydrolysed product may be a single substance containing both chemically-bound water and the organic hydroxy compound or it may be a mixture of, for example, wholly hydrolysed and unhydrolysed molecules of the original complex phosphate. Polymerisation of the hydrolysis product may accompany hydrolysis so that higher molecular weight products of the invention are formed. Hydrolysis may be effected by any convenient means, but for many of the compounds of the invention it is sufficient to add water at room temperature or to keep the compounds in contact with moist air for a sufficient time. Conveniently this is done by fluid-

ising the compound in a stream of humidified air, preferably at a temperature below 80°C.

The complex phosphate may be used without isolation from the mixture from which it is formed or after removal of part of the reaction products.

Thus the crude reaction product mixture of the process employed may be used directly for at least some of the applications hereinafter described, for example, the coating of metals. Alternatively, a solid comprising the complex phosphate may be separated from the reaction mixture and used as such or optionally further purified before use. Separation of the product may be effected by any convenient means, for example by precipitation by cooling, evaporation of volatile constituents or addition of a further component, followed by filtration or by chromatography. In some cases spontaneous precipitation of the product from the reaction mixture occurs, and separation is effected simply by filtration. The product may be washed, for example with ethanol. The mother liquor left after separation of the product may be discarded or recycled for further use, preferably after purification from unwanted side-products of the reaction.

The complex phosphates according to the invention decompose on heating to give aluminium phosphate in amorphous or various crystalline forms. The temperature at which aluminium phosphate forms depends upon the particular complex phosphate heated, but is normally from 80°C to 500°C, and is often below 100°C. It is convenient to heat the complex phosphate to a temperature from 100°C to 150°C to form aluminium phosphate. Surprisingly, crystal forms of aluminium phosphate can be obtained at low temperatures which are normally obtained only by heating aluminium phosphate to temperatures in excess of 800°C. The aluminium phosphate may be further heated, for example to change its crystalline form. When the gram atom ratio of aluminium to phosphorus in the complex phosphate is 1:1 the aluminium phosphate produced has the same ratio of aluminium to phosphorus and is consequently particularly chemically stable.

The invention thus provides a method for producing aluminium phosphate in many desirable forms at low temperatures, conveniently from solutions of the complex phosphates in water or organic solvents. The complex phosphates of the invention are therefore especially useful in providing means for producing, for example, formed bodies, coatings and binders comprising aluminium phosphate. The properties of aluminium phosphate are such as to confer on these materials desirable properties such as strength, refractoriness or chemical inertness.

Solutions of complex phosphates according to the invention may conveniently comprise additional components, for example materials

which will aid the further processing of the solutions or desirably affect the products formed from the solutions. Thus organic materials, especially polymers, for example hydroxypropyl cellulose or a polyamide, may be dissolved in the complex phosphate solution, especially in cases where the solvent is an organic solvent. Additional components, for example pigments, colorants or fillers, may likewise be dispersed in the solutions of the complex phosphates. It is especially preferred that the solution of complex phosphate comprises a material or materials which control the physical nature of the solid phase of aluminium phosphate which is produced from the solution, for example by heating. When the solvent comprises water it is preferred to use a crystallisation stabiliser, for example finely divided silica or alumina, or a nucleation activator or catalyst, for example dibutyl peroxide, or calcium, magnesium or sodium chloride. When the solution of the complex phosphate is non-aqueous, for example when the solvent is ethanol, it is preferred to use a boric acid ester or ether or a silicic acid ester or ether, for example methyl borate, trimethoxy boroxine or ethyl silicate to suppress the crystallisation of aluminium phosphate.

Solutions of the complex phosphates, especially aqueous solutions, are viscous, so that fibres may be prepared from them by one of the usual fiberising processes such as drawing, blowing, extrusion through a spinneret or centrifugal spinning. The use of the solutions in the preparation of aluminium phosphate fibres is described in our copending U.K. patent application 2791/73 (Serial No. 1,322,725), which has been divided out of the present application.

Solutions of the complex phosphate in water or organic solvents may also be used to produce coatings of aluminium phosphate for a number of surfaces, by removal of solvent and preferably heating of the deposited coating. The use of the solutions in the coating of surfaces is described in our copending U.K. patent application 3344/73 (Serial No. 1,322,726) which has been divided out of the present application.

Furthermore, a solution comprising one or more of the complex phosphates may be used as an adhesive or binder for a wide variety of materials. It is especially useful as an adhesive or binder for siliceous materials, for example sand or glass; metal especially metal powders and ceramic materials generally, for example alumina or carbon. The adhesive bond may be strengthened by heating, preferably to temperatures between 200°C and 1000°C, after removal of solvent and initial curing at 100°C to 200°C of the adhesive or binder.

Strong, thermally stable and chemically inert resistant composite materials may be prepared by incorporating aligned or random fibres, for example glass fibre, carbon fibre, silicon car-

- 5 bide fibre or asbestos with a desired quantity of a solution of the complex phosphates in water or a polar solvent, removal of the solvent, initial curing at 100°C to 200°C and preferably further heating, for example to a temperature of from 200°C to 1000°C.

- 10 The complex phosphates may also be used to prepare fine particles of aluminium phosphate by rapid heating of the bulk material to a temperature greater than 900°C, and grinding the resultant mass. Fine particles produced in this way may advantageously be used as a reinforcing filler in polymers such as polyvinyl chloride or they may be incorporated into molten glass as a nucleating agent in the preparation of nucleated glass.

- 15 The invention is illustrated but not limited by the following Examples:—

Example 1

- 20 40 gram of anhydrous aluminium chloride was added to 300 ml of laboratory grade ethyl alcohol. The resultant solution was cooled to

0°C and 18.6 ml of 88% orthophosphoric acid was added to it in a drop-wise manner and the reaction mixture stirred. The reaction was carried out in an atmosphere of dry nitrogen. The white crystalline material formed was separated from the mixture, washed with ethanol and dried under vacuum at a temperature of 0°C. 70 gram of product was obtained.

The product compound had the empirical formula $\text{AlPClH}_{2.2}\text{C}_5\text{O}_8$ and on a dry basis gave the following chemical analysis (expressed as a percentage by weight):

Al	P	Cl	C	H
7.87	9.04	10.34	28.03	7.35

and contained 53.76% by weight of chemically-bound ethyl alcohol. The infra-red absorption spectrum of the compound containing a trace of water was measured using the liquid paraffin mull technique. The principal band positions are given in Table I which indicates the relative strengths of the bands.

TABLE I

Band positions in reciprocal centimetres

3450	strong	970	weak
1920	weak	935	weak
1635	weak	900	medium strong
1230	very strong	870	medium strong
1100	strong	800	weak
1075	strong	715	medium strong
1030	very strong		

A specially dried sample gave infra-red absorption spectrum band positions shown in Table II:

TABLE II

Band positions in reciprocal centimetres

3450	medium strong	905	strong
3100	strong	880	strong
1235	very strong	660	medium strong
1110	very strong	625	medium strong
1095	} medium strong	520	strong
1085			
1045	very strong	390	medium strong

The X-ray powder data were also obtained for the compound containing a trace of water, using a Philips powder camera, $\text{CuK}\alpha$ radiation

and a nickel filter. The intensities were obtained by visual observation. The data obtained are shown in Table III:

TABLE III
X-ray powder data

dÅ	I/I ₀	dÅ	I/I ₀	dÅ	I/I ₀
10.7	vs	2.94	vw	2.097	vvw
7.2	vw	2.89	vvw	2.034	vvw
6.25	w	2.81	w	1.967	vvw
5.24	w	2.72	vvw	1.951	vvw
4.87	w	2.64	vw	1.899	vvw
4.57	vw	2.60	vvw	1.866	vvw
4.04	m	2.54	vvw	1.786	vvw
3.62	s	2.489	vw	1.660	vvw
3.44	s	2.460	vvw	1.627	vvw
3.25	vvw	2.279	vw	1.594	vvw
3.18	vw	2.236	vvw	1.553	vvw
3.11	vvw	2.174	vvw	1.528	vvw
3.02	w	2.132	vvw		

s = strong; v = very; w = weak; m = medium.

A differential thermal analysis was carried out on a sample of the compound which contained a small quantity of water. The thermogram covered the range 0–800°C and was carried out under nitrogen. Sharp endothermic peaks at 82°C and 96°C and a broad endothermic inflection at approximately 175°C were observed.

Example 2

10 gram of the compound produced in Example 1 was placed in a tray to a depth of $\frac{1}{4}$ -inch and left for 24 hours at a temperature of 20°C and in a relative humidity of 75%. The compound lost 16% of its weight to yield another compound which was amorphous. The content of chemically-bound ethyl alcohol had fallen to 26% by weight and the amount of chemically-bound water had increased to 22% by weight. The compound contained 10.84% by weight of aluminium 12.25% by weight of phosphorus and 12.75% by weight of chlorine.

Example 3

26.7 gram of anhydrous aluminium bromide were dissolved in a mixture of 100 ml of absolute ethyl alcohol and 9.8 gram of 88% orthophosphoric acid. The mixture was warmed gently to assist dissolution and the final clear liquid allowed to cool. After a short period of time a crystalline precipitate was formed. This was filtered off and dried in a vacuum desiccator. The chemical analysis of the crystals was as follows:

	Al	Br	P	$\text{C}_2\text{H}_5\text{OH}$	H_2O
% by weight	6.8	20.3	7.6	47.0	0.7

On a dry basis, the crystals have an empirical formula of $\text{AlPBrH}_2\text{C}_2\text{O}_8$. X-ray powder data on the crystals were obtained using a Philips powder camera, $\text{CuK}\alpha$ radiation and a nickel filter, the intensities being obtained by visual observation. The data are shown in Table IV:

Table IV		Table IV (continued)		
	Intensity	Value	Intensity	Value
5	s + +	10.773	m - -	2.996
	vvvw	8.927	vw	2.967
	w	7.824	w - vw	2.892
	w	7.339	w - w +	2.838
	w - w +	6.189	vw	1.564
10	vvw	5.786	s=strong; v=very; w=weak; m=medium	
	m -	5.368		
	w - w +	4.911		
	w - w -	4.692		
	vvw -	4.414		
15	m - m -	4.130	A differential thermal analysis was carried out over the range 0—800°C under nitrogen. A sharp endothermal peak at 108°C and a broad endothermal inflection at about 175°C were observed.	
	m + - m + +	3.682		
	vw	3.573		
	m + +	3.490		
	w - w +	3.241		
	w	3.151	The infra-red absorption spectra of the compound was measured using the liquid paraffin mull technique. The principal band positions are shown in Table V:	
	m - -	3.066		

TABLE V

Band position in reciprocal centimetres

3450	medium strong	1038	very strong
3140	strong	902	strong
1414	medium strong	880	strong
1240	very strong	615	medium strong
1112	very strong	520	strong
1090	} medium strong	385	weak-medium strong
1080			

Example 4

26.7 gram anhydrous aluminium chloride was dissolved in 700 ml of n-propyl alcohol and to this solution 19.6 gram 88% orthophosphoric acid was added to give a clear solution.

To this solution a large excess of specially dried diethyl ether was added. A white amorphous precipitate was formed, which was filtered off and dried. The material had the following analysis:

	Al	Cl	P	H ₂ O	n-propyl alcohol
% by weight	10.7	7.6	12.1	3.6	32.2

Example 5

13.4 gram of anhydrous aluminium chloride was dissolved in 100 ml of n-decanol, and to the solution 9.8 gram of 88% orthophosphoric

acid was added. The reaction mixture was filtered. A large excess of diethyl ether was added to the filtrate and a white produce was precipitated, having the following analysis:

	Al	Cl	P	H ₂ O	n-decanol
% by weight	10.4	10.7	13.4	20.8	10.7

Example 6

40.05 gram anhydrous aluminium chloride was dissolved in 250 ml of isopropyl alcohol. 29.4 gram of 88% orthophosphoric acid was

added to give a clear solution. The addition of a large excess of diethyl ether to this solution resulted in the precipitation of a white amorphous solid having the following analysis:

		Al	Cl	P	H ₂ O	isopropyl alcohol
10	% by weight	10.9	13.7	12.3	22.7	13.5

When specially dried diethyl ether was used the product had the following analysis:

		Al	Cl	P	H ₂ O	isopropyl alcohol
	% by weight	10.7	8.3	11.9	15.2	31.7

Example 7

15 The compound prepared as described in Example 1 was dissolved in a number of sol-

vents and each saturated solution was analysed. The results obtained are shown in Table VI:

TABLE VI

Solvent	Solubility	Analysis				
	g solid/100 ml solvent	Al	PO ₄	Cl	C ₂ H ₅ OH	Solvent
N-pentanol	10	0.86	3.04	1.13	5.90	89.07
Ethanol	11	0.96	3.39	1.26	94.39	—
Isopropanol	26	1.96	6.90	2.57	13.37	75.20
Methanol	90	4.19	14.75	5.50	28.60	46.96
Water	1000	7.15	25.19	9.40	48.88	9.38

Example 8

20 A clear solution was obtained by dissolving 26.7 gram of anhydrous aluminium chloride in 200 ml of methanol and adding 19.6 gram of 88% orthophosphoric acid. This solution was concentrated by evaporation to a thick syrup, useful as a coating solution hereinbefore described.

Example 9

6.64 gram of dry hydrochloric acid gas was dissolved in 185 gram of isopropyl alcohol and 33.1 gram of ethyl alcohol. To this solution 17.9 gram of 88% orthophosphoric acid was added. To this resultant solution 37.25 gram of aluminium isopropoxide was added and stirred to dissolve. The solution was filtered and the filtrate had the following chemical analysis:

		Al	Cl	P	H ₂ O	organic solvent
	% by weight	2.1	2.2	2.1	2.6	86.7

Example 10

40 400 gram of anhydrous aluminium chloride was dissolved in 3000 ml of absolute ethanol and the solution cooled in ice to a temperature of 0°C. 325 gram of 88% orthophosphoric acid was slowly added to the solution with stirring. 370 gram of a white crystalline solid with the empirical formula $\text{Al}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{O}_8$ was filtered off and dried in a vacuum oven at 20°C for two hours.

50 A solution of 800 gram of this solid in 100 gram of water was prepared; the solution had a viscosity of 700 poise.

Monofilaments were drawn from the solution into air at a temperature of 20°C. The collected monofilaments were dried at 120°C and transferred to an oven at 500°C where they were kept for 4 hours. The resulting product consisted of clear fibres of essentially aluminium phosphate.

Example 11

The crystalline solid of empirical formula $\text{Al}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{O}_8$ was prepared as described in Example 10.

800 gram of the solid was dissolved in 150 ml of water to give a solution having a viscosity of 20 poise.

This solution was introduced into a centrifuge spinning device (a "candy-floss" machine) in which it was spun. Fibres of diameter from 5 micron to 15 micron were readily produced. They were placed in an oven at 500°C for 30 minutes, after which time they were clear fibres consisting essentially of aluminium phosphate.

Example 12
A concentrated (approximately 5 molar)

solution of the compound prepared as described in Example 10 was made up in water. This had a viscosity of 2600 poise, and from it continuous monofilaments were drawn from a spinneret. On heating, the monofilaments lost about 45% in weight. The monofilaments (mean diameter 15 microns) were clear and

were shown by X-ray analysis to be essentially crystalline aluminium phosphate. Table VII shows the analysis of the filaments produced and the results of the particular heating treatment given to each sample.

TABLE VII

Sample	Weight % Al	Weight % PO ₄	Weight % Cl	Heat Treatment		X-Ray Examination	Comments	% Weight loss on heat treatment
				Time Hrs	Temp °C			
A	18.2	68.0	2.0	2	250	Major phase cristobalite, minor phase tridymite	Thin fibres, clear	Not determined
B	17.56	70.05	2.86	16½	250	Major phase tridymite, minor phase cristobalite	Thin fibres, clear	44.03
C	20.97	75.33	0.25	2	500;550	Major phase cristobalite, minor phase tridymite	Thin fibres, clear	46.21
D	21.00	72.87	0.28	5	700	Major phase tridymite, minor phase cristobalite	Thin fibres, clear	45.13
E	19.86	79.49	Not detected	4	900—950	Major phase tridymite, minor phase cristobalite	Thin fibres, clear	46.29

Example 13
A solution was prepared as in Example 12 and various additional components added to portions of the solution. Filaments of about 10 microns diameter were drawn from each portion and samples were heated for different times. The filaments were examined by X-ray diffraction. The results obtained are shown in Table VIII:

TABLE VIII
The Effect of Various Additives on the Crystallisation of $AlPO_4$ Fibres

Addition to Solution	Firing Temp °C	Time at Temp Hrs	X-Ray Examination
Nil	200 400 800 1000	3 3 3 3	Largely non-crystalline + trace of tridymite } <i>very different</i> Largely non-crystalline + trace of tridymite Some non-crystalline + tridymite (major phase) + cristobalite (minor phase) Mainly crystalline, largely cristobalite + some non-crystalline
5% $AlCl_3$	200 400 800 1090	3 3 3 3	Non-crystalline Largely non-crystalline + trace crystalline too weak to identify Largely non-crystalline + trace of tridymite Some non-crystalline + tridymite and cristobalite ($> 10^{-5}$ cm)
Alumina hydrate	200 400 800 1090	3 3 3 3	Largely non-crystalline ($< < 10^{-5}$ cm) + trace tridymite ($> 10^{-5}$ cm) Largely non-crystalline + slightly more tridymite than fired 200 °C Some non-crystalline + tridymite ($> 10^{-5}$ cm) Some non-crystalline + tridymite and cristobalite ($> 10^{-9}$) More crystallinity than 200 and 400 °C
5% H_3PO_4	200 —200 400 800 1090	3 3 3 3 3	Non-crystalline material present. Cristobalite + Berthelinite present Some non-crystalline present. Crystalline phase present in Berthelinite ($> 10^{-5}$ cm) Highly crystalline, any non-crystalline phase low concentration. Major crystalline phase Berthelinite + Cristobalite Highly crystalline, major phase cristobalite + trace Berthelinite + trace unidentified phase ($> 10^{-4}$ cm)
5% SiO_2 (Silica Sol.)	200 400 800 1090	3 3 3 3	Largely non-crystalline ($< < 10^{-5}$ cm) + trace tridymite ($> 10^{-5}$ cm) Large proportion non-crystalline + tridymite ($> 10^{-5}$) Some non-crystalline. Major phase is tridymite + very minor amount cristobalite ($> 10^{-5}$ cm) Some non-crystalline + tridymite and cristobalite ($> 10^{-9}$) (similar to ACPH + 5% alumina with slightly lower proportion of crystalline material)

*than 1000
V11*

- Example 14
- A 30% by weight aqueous suspension of a colloidal graphite was prepared. To 100 ml of this was added 50 gram of the compound prepared as described in Example 10 and the suspension well mixed. The suspension was extruded at 25°C through a spinneret having an aperture of 1/100 inch and the resultant monofilament drawn down to 10 microns. The filament drawn down was heated for 1 hour at 150°C and then at 800°C for 3 hours under nitrogen. The final filament comprised aluminum phosphorus in the cristobalite form and about 60% by weight of aligned graphite platelets.
- Example 15
- Solutions of the compound prepared as described in Example 1 were made up in methanol and isopropyl alcohol. To portions of each solution, ethyl silicate was added and dissolved. Solutions with and without ethyl silicate were evaporated to dryness at 120°C and the solids formed were ground to a fine powder. This powder was then heated at various temperatures for various periods of time and the products examined by X-ray diffraction techniques. The results of the inclusion of ethyl silicate on the crystallization of aluminum phosphorus from the solutions is shown in Table IX:

TABLE IX
The effect of Ethyl Silicate on the Crystallization of AlPO_4 powders

Heating Temperature °C	Heating Time Hrs	Isopropyl Alcohol Solutions		Methanol Solutions	
		containing ethyl silicate	no ethyl silicate	containing ethyl silicate	no ethyl silicate
200	2	Largely non-crystalline (size $< 10^{-5}$ cm)	Non-crystalline	—	—
300	3	—	—	Non-crystalline	Non-crystalline
400	2	Non-crystalline	Non-crystalline	—	—
600	3	—	—	Non-crystalline	Non-crystalline
800	2	Non-crystalline	Largely non-crystalline + trace tridymite $\leq 10^{-5}$	—	—
1000	2/3	Largely non-crystalline + trace of a crystalline material too weak to identify	Highly crystalline AlPO_4 cristobalite + tridymite phase. Average crystal size $\geq 10^{-5}$ cm	Non-crystalline	Highly crystalline AlPO_4 cristobalite + tridymite forms. Average crystallite size $\geq 10^{-5}$ cm

Example 16

A 10% by weight solution of the compound prepared as described in Example 1 in methanol was applied to a glass fibre immediately after it had been drawn. The coated glass fibre was then heated for 1 hour at 150°C. The tensile strength of the coated glass fibre was 50% higher on average than that of the uncoated glass fibre drawn at the same time and under the same conditions.

Example 17

A solution containing 2% by weight of the compound prepared as described in Example 1 was made up in ethyl alcohol and to it was added 0.1% by weight of a wetting agent. Glass slides were then dipped into the solution, drained and heated at the following temperatures — 120°C, 250°C, 350°C, 450°C and 550°C for 2 hours. The slides were immersed in a suspension of cement in water. No reduction in the thickness of the film of aluminium

phosphate on the glass occurred, as examined microscopically and gravimetrically, after 65 hours of immersion at 20°C.

Example 18

The crystalline solid of empirical formula $\text{AlPClH}_{25}\text{C}_8\text{O}_8$ was prepared as described in Example 10.

10 gram of the solid was dissolved in 100 ml of ethanol. Carbon fibres were immersed in the solution, withdrawn and dried, first in air and then at 150°C for 15 minutes. The fibre, which was found to have absorbed 5% of its weight after this treatment, was heated at 950°C for 5 hours in an atmosphere of dry nitrogen.

Similar weights of untreated carbon fibre and carbon fibre coated as above were treated for 2 hours in a stream of air. Table X shows the loss of weight of the carbon fibre samples when heated at four different temperatures and illustrates the protection against oxidative degradation afforded by the coating.

TABLE X

Loss of weight of coated and uncoated carbon fibre

Temperature °C	Uncoated fibre + weight loss in 2 hours	Coated fibre % weight loss in 2 hours
300	0	0
400	0	0
500	19	1.3
700	100	3.9

Example 19

Carbon fibre was degreased by immersion in trichloroethylene and passed through solutions of the compound prepared as described in Example 1 in three different solvents, water, ethyl

alcohol and methanol. The fibre was dried at 250°C and the coating cured by further heating at 500°C. The increased resistance to oxidation of the carbon fibre as a result of the coating is shown in Table XI:

TABLE XI

Coating Solution	Deposit % w/w *	% Loss in Weight after Heating in Air for 2 hours		
		500°C	600°C	700°C
2% complex in water	—	1.3	12.9	99.8
10% complex in water	2	0.7	99.1	89.4
2% complex in methanol	<0.1	1.3	27.5	96.9
10% complex in methanol	2	0	18.5	97.3
2% complex in ethanol	0.6	1.1	12.5	98.8
8.7% complex in ethanol	4.7	1.1	21.7	97.6
Double coating with 2% solution complex in ethanol	4.4	0	14.1	91.6
UNTREATED FIBRE	—	56.4	100	100

* after drying at 250°C.

Example 20

Carbon fibre was coated with 4% by weight of aluminium phosphate by treatment as in Example 19 with a 2% by weight solution of complex phosphate in ethyl alcohol. The weight loss of the coated fibre compared with

that of an uncoated fibre when they were both heated at 600°C in air was recorded at intervals of time. The results obtained are shown in Table XII, showing that the rate of oxidation is very considerably reduced by the presence of the coating.

TABLE XII

Time at 600°C in air (minutes)	Weight loss % w/w	
	uncoated fibre	coated fibre
15	60.6	5.4
30	97.1	7.9
45	98.5	9.0
60	99.6	10.1
75	100	10.1

Example 21

The mechanical properties of uncoated carbon fibre and fibre coated as described in Example 20 were compared by measuring their Young's modulus and tensile strength. The re-

sults shown in Table XIII were obtained, showing the beneficial effect of the coating on the mechanical properties after exposure of the fibre to oxidising conditions.

TABLE XIII

Fibre and treatment	Modulus lbf/in ²	Tensile Strength lbf/in ²
(1) Uncoated Fibre	25—28 × 10 ⁶	28—29 × 10 ⁴
(2) Uncoated Fibre heated in air 10 minutes at 600°C	— too fragile to test —	
(3) AlPO ₄ coated (4%)	22—25 × 10 ⁶	21—35 × 10 ⁴
(4) As (3) but heated in air 10 minutes at 600°C	29 × 10 ⁶	20 × 10 ⁴
(5) AlPO ₄ coated (3.6%)	23—33 × 10 ⁶	18—34 × 10 ⁴
(6) As (5) but heated in air 10 minutes at 600°C	21—23 × 10 ⁶	12—14 × 10 ⁴

Example 22

Carbon fibre was passed through molten aluminium. Only a few isolated globules of aluminium adhered to the fibre. Carbon fibre coated with 2% of aluminium phosphate by the process described in Example 20 was similarly passed through molten aluminium. It emerged with a continuous and adherent film of aluminium metal on its surface.

20 WHAT WE CLAIM IS:—

1. A halogen-containing complex phosphate of aluminium containing at least one chemically-bound molecule of a hydroxy compound R—OH wherein R is an organic group.
2. A complex phosphate as claimed in claim 1 wherein R is an aliphatic hydrocarbon group.
3. A complex phosphate as claimed in claim 1 wherein R is a substituted aliphatic hydrocarbon group.
4. A complex phosphate as claimed in claim 2 or claim 3 wherein the hydroxy compound is an aliphatic alcohol containing 1—10 carbon atoms.
5. A complex phosphate as claimed in claim 4 wherein the hydroxy compound is an aliphatic alcohol containing 1—4 carbon atoms.
6. A complex phosphate as claimed in claim 5 wherein the hydroxy compound is ethyl alcohol.
7. A complex phosphate as claimed in any of the preceding claims wherein the halogen is chlorine.
8. A complex phosphate as claimed in any of claims 1 to 6 wherein the halogen is bromine.

9. A complex phosphate as claimed in any of the preceding claims wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of phosphorus is substantially 1:1.

10. A complex phosphate as claimed in any of the preceding claims wherein the ratio of the number of gram atoms of aluminium to the number of gram atoms of halogen is substantially 1:1.

11. A complex phosphate as claimed in any of the preceding claims containing from 1—5 molecules of a hydroxy compound.

12. A complex phosphate as claimed in claim 11 containing 4 molecules of a hydroxy compound.

13. A complex phosphate as claimed in any of the preceding claims containing chemically-bound water and a chemically-bound organic hydroxy compound.

14. A complex phosphate as claimed in claim 13 wherein the total number of molecules of water and of the organic hydroxy compound is from 2—5.

15. A complex phosphate as claimed in claim 1 having the empirical formula $\text{AlPClH}_2\text{C}_4\text{O}_8$.

16. A complex phosphate as claimed in claim 1 having the empirical formula $\text{AlPBrH}_2\text{C}_4\text{O}_8$.

17. A method of preparing a complex phosphate claimed in any of the preceding claims or a mixture containing the said complex phosphate comprising the step of reacting aluminium compound with an organic hydroxy compound R—OH and phosphoric acid and,

- when a compound of aluminium other than a halide is used, a halogen acid.
18. A method as claimed in claim 17 wherein R of the hydroxy compound is an aliphatic hydrocarbon group. 5
19. A method as claimed in claim 17 wherein R of the hydroxy compound is a substituted aliphatic hydrocarbon group.
20. A method as claimed in claim 17 wherein the hydroxy compound is an aliphatic alcohol containing 1—10 carbon atoms. 10
21. A method as claimed in claim 20 wherein the aliphatic alcohol contains 1—4 carbon atoms.
22. A method as claimed in claim 21 wherein the aliphatic alcohol is ethyl alcohol. 15
23. A method as claimed in claim 21 wherein the aliphatic alcohol is methanol.
24. A method as claimed in any of claims 17 to 23 wherein the aluminium compound is an aluminium halide. 20
25. A method as claimed in claim 24 wherein the aluminium halide is aluminium chloride.
26. A method as claimed in claim 24 wherein the aluminium halide is aluminium bromide. 25
27. A method as claimed in any of claims 17 to 26 wherein the aluminium compound is added to the hydroxy compound and phosphoric acid is reacted with the resultant mixture. 30
28. A method as claimed in any of claims 17 to 27 wherein the aluminium compound is dissolved in a suitable solvent before reaction.
29. A method as claimed in any of claims 17 to 28 wherein the molar ratio of aluminium to phosphorus in the reaction is substantially 1:1. 35
30. A method as claimed in any of claims 17 to 29 wherein the reaction is carried out at a temperature below 60°C.
31. A method as claimed in claim 30 wherein the reaction is carried out at a temperature from 0°C—50°C. 40
32. A method of preparing a halogen-containing complex phosphate of aluminium as claimed in claim 1 substantially as described herein. 45
33. A method of preparing a halogen-containing complex phosphate of aluminium substantially as described in any one of Examples 1 to 6, 8 and 9. 50
34. A complex phosphate or a mixture containing said complex phosphate whenever made by a method claimed in any of claims 17 to 23.
35. A method of preparing a homogeneous composition comprising a phosphate of aluminium and an organic solvent which comprises dissolving in an organic solvent a complex phosphate as claimed in any of claims 1 to 16 and 34. 55
36. A method as claimed in claim 35 wherein the organic solvent is a polar organic solvent. 60
37. A method as claimed in claim 36 wherein the polar organic solvent is an oxygen-containing polar organic solvent.
38. A method as claimed in claim 37 wherein the oxygen-containing polar organic solvent is an aliphatic alcohol containing 1—5 carbon atoms. 65
39. A method as claimed in claim 38 wherein the aliphatic alcohol is methanol or ethyl alcohol. 70
40. A composition comprising a phosphate of aluminium and an organic solvent whenever prepared by any of claims 35 to 39.
41. A composition as claimed in claim 40 comprising an organic polymer. 75
42. A composition as claimed in claim 41 wherein the organic polymer is hydroxy propyl cellulose.
43. A composition as claimed in claim 41 wherein the organic polymer is a polyamide. 80
44. A composition as claimed in claim 40 comprising a boric acid ester or ether or a silicic acid ester or ether.
45. A composition as claimed in claim 44 wherein the boric acid ester or ether is methyl borate or trimethoxy boroxine. 85
46. A composition as claimed in claim 44 wherein the silicic acid ester is ethyl silicate.

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